

Diurnal Variations of Hydroxyl in the Stratosphere and Mesosphere Derived from AURA MLS

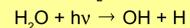
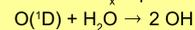


Diurnal variations in hydroxyl (OH) in the stratosphere and mesosphere have been analyzed using measurements from the Aura Microwave Limb Sounder (MLS). The primary driver for OH diurnal variations is the ultraviolet actinic flux that initiates photochemical reactions which produce OH. The magnitude of this flux is governed largely by changes in solar zenith angle (SZA) throughout the day, and OH diurnal variations are well approximated by an exponential function of the secant of SZA: $[OH] \sim \exp[-\beta \sec(SZA)]$, where the parameter β is a function of altitude. We examine the magnitude of β and show that it is related to the optical depths of ultraviolet absorption by ozone and oxygen. Comparison between β values derived from MLS measurements and those from SLIMCAT model simulations shows very good agreement. The vertical profile of β from MLS can also be represented by an analytic formulation involving the ozone and water vapor photodissociation rates.

Introduction

Photochemistry:

- HO_x = odd hydrogen = sum of (OH, HO_2 , and H) $\sim OH + HO_2$ in the stratosphere
- Chemical lifetime of HO_x is \sim minutes to an hour, so photochemical steady-state is assumed and transport of HO_x is neglected.
- Production of HO_x is primarily from the reactions



(leads to dependence on solar UV, Ozone (O_3), and water vapor (H_2O))

- Loss of HO_x is primarily from the reaction $OH + HO_2 \rightarrow H_2O + O_2$

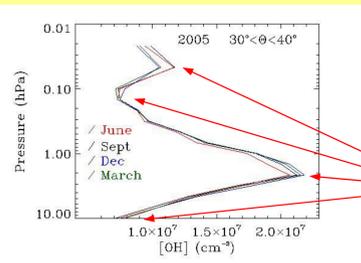
(leads to a square root dependence of OH concentration on source terms)

First-order expression for OH variations:

Based on the discussion in *Canty and Minschwaner* [2002],

$$\frac{dOH}{OH} = 0.5 \left[\frac{dH_2O}{H_2O} + \frac{dO_3}{O_3} + \frac{dI}{I} - \tau_{O_3} \frac{dN_{O_3}}{N_{O_3}} - \bar{\tau} \frac{d \sec(SZA)}{\sec(SZA)} \right] \quad (\text{eq 1})$$

where I =solar UV irradiance, N_{O_3} =ozone overburden, τ_{O_3} =ozone optical depth, $\bar{\tau}$ = mean optical depth for O_3 or H_2O photodissociation, and $\sec(SZA)$ =secant of the local solar zenith angle. Fractional variations in OH should be half as large as fractional changes in UV irradiance, H_2O , O_3 , N_{O_3} , and $\sec(\theta)$ (assuming all τ 's ~ 1).



We use measurements from the Microwave Limb Sounder (MLS) on the Aura satellite to test the validity of eq 1. At left are four vertical profiles of mean OH measured by MLS within a limited θ range.

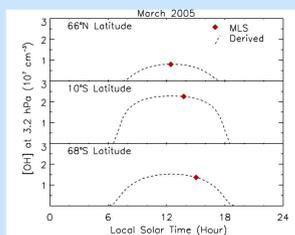
Initially, four pressures are examined – representing the bottom, stratospheric peak, stratopause minimum, and mesospheric peak in the OH profile.

Solar Zenith Angle Dependence, I

Parameterized Approach

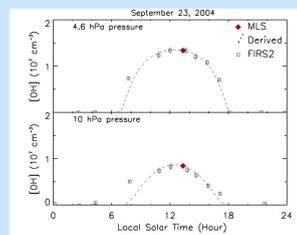
(Described in Minschwaner et al., *The photochemistry of carbon monoxide in the stratosphere and mesosphere evaluated from MLS observations*, JGR, 2010)

The figures below show results from an observationally-based diurnal estimation of OH using MLS measurements. Assume constant values for H_2O , O_3 , and N_{O_3} throughout the day, and $OH(t) = OH_0 \exp[-0.5 \tau_{O_3} \sec(\theta(t-\phi))]$, where t =time, θ =solar zenith angle at phase lagged time $t-\phi$, τ_{O_3} =ozone optical depth using weighted mean cross section $\sigma=1.2 \times 10^{-18} \text{ cm}^2$, and OH_0 =peak daytime OH concentration. Both OH_0 and τ_{O_3} are determined using MLS measured OH and O_3 .



MLS OH at 3.2 hPa for three latitudes and local times (diamonds). Dashed curves show parameterized diurnal variations using coincident O_3 measured by MLS.

- **Advantage:** Permits estimation over most of the diurnal range using a single daytime measurement of OH and O_3 .
- **Disadvantages:** Assumes a priori functional form. Use of a mean ozone cross section limits the applicable altitude range to the middle/upper stratosphere (10 - 1 hPa).



MLS OH at 4.6 and 10 hPa (diamonds) for overpass during a balloon flight from Fort Sumner, NM. Dashed curves are parameterized diurnal variations, squares are FIRS-2 observations (data courtesy K. Jucks).

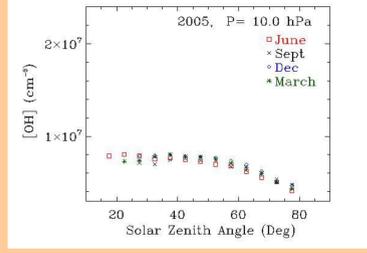
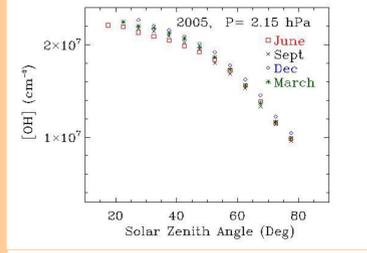
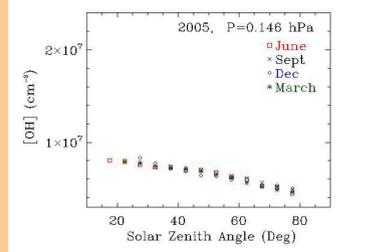
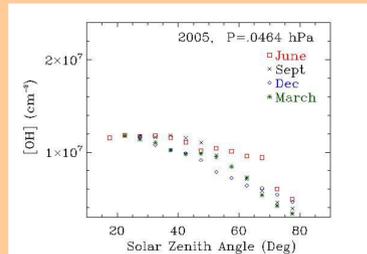
Solar Zenith Angle Dependence, II

Statistical Approach

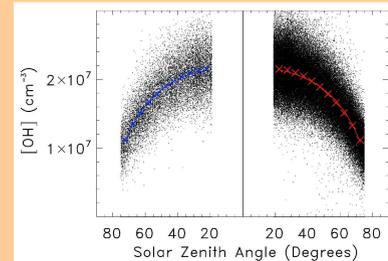
(Described in Minschwaner et al., *Hydroxyl in the stratosphere and mesosphere – part I: diurnal variability*, ACPD, 2010)

This approach exploits the fact that MLS OH profiles are spread over a large range in latitude, longitude, and local time (thus, SZA). To minimize effects from spatial or temporal variations in H_2O and O_3 concentrations, filter the OH data at each pressure level by including only those data for which the simultaneous MLS measurements of H_2O and O_3 are within $\pm 20\%$ of the monthly mean value at that pressure level. In this way, filtering by H_2O and O_3 approximates a partial derivative in eq (1).

The plots below show MLS monthly mean OH as a function of solar zenith angle for four pressure levels and four months. Each data point represents a mean composed of ~ 1000 to 2000 measurements over a range of latitudes from 50°S to 60°N .



The figure below shows individual OH measurements at the 2.15 hPa level (near the stratospheric peak) for 2006. Morning data are shown to the left of the 0° line; afternoon data are to the right. Blue (red) x's indicate mean values within 5° SZA bins for the morning (afternoon). The diurnal asymmetry is small ($<3\%$) at this pressure level.

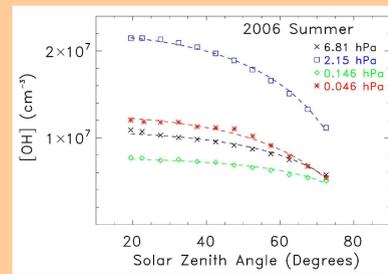


The mean values can be accurately fit with a two-parameter exponential function

$$OH(SZA) = OH_0 \exp[-\beta \sec(SZA)] \quad (\text{eq 2})$$

where β describes the steepness of the SZA dependence, and OH_0 determines the overall level. Both of these parameters are pressure (altitude) dependent.

The figure below shows OH concentrations at 6.81 hPa (black x's), 2.15 hPa (blue squares), 0.146 hPa (green diamonds), and 0.046 hPa (red *s) obtained from full day (morning plus afternoon) averages within 5° solar zenith angle bins. Corresponding dashed curves show exponential function fits using eq (2).

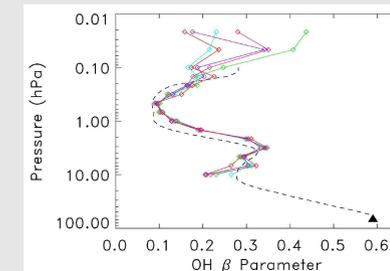


Key Points:

- The OH - SZA relationship generally shows little seasonal dependence except at the highest pressure level (0.046 hPa). Note that the S/N is also reduced at this level.
- OH diurnal variations derived using the statistical approach match the functional form used in the parameterized (both are exponential functions of SZA)
- A simple two-parameter fit (eq. 2) can capture the observed diurnal variability of OH means to within $\pm 5\%$

The β Parameter for OH Diurnal Variations

The figure below displays vertical profiles of the parameter β_{OH} (representing the steepness of the OH-SZA fit, eq. 2) from MLS measurements during the NH summer of 2004 (green), 2005 (cyan), 2006 (violet), 2007 (red), and 2008 (orange). Dashed curve shows β_{OH} derived from simulations of the SLIMCAT model for 2005. Solid triangle shows β_{OH} value determined from a fit to the aircraft OH measurements by Hanisco et al (2001).

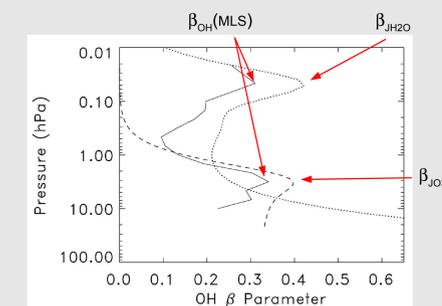


The vertical profile of β_{OH} is related to the diurnal variation of photolysis. Consider an approximation to the square-root of the photolysis frequency

$$\sqrt{J} = \sqrt{J_0} \exp[-0.5 \beta_j \sec(SZA)] \quad (\text{eq 3})$$

We calculate vertical profiles of J_{O_3} and J_{H_2O} using a full radiative transfer model, then evaluate the corresponding β_j using eq 3.

The plot below shows the mean β_{OH} from 2004-2008 MLS OH NH summer measurements (solid), along with derived values of β_j from ozone photodissociation (dashed) and water vapor photodissociation (dotted), assuming a square-root dependence on HO_x production as described above.



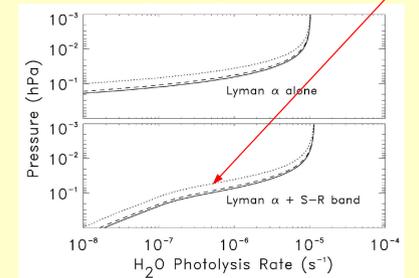
Key Points:

- Mean values of β are between 0.1 and 0.4
- Distinctive vertical variation in β shows remarkable consistency from year to year.
- Agreement between MLS β and SLIMCAT OH β is very good; SLIMCAT β in lower stratosphere also agrees well with β derived from aircraft OH data.
- Vertical variations in MLS β_{OH} are broadly consistent with photodissociation β_j of ozone in stratosphere, and water vapor in mesosphere.

Implications for photodissociation of water vapor and ozone

OH diurnal variations observed by MLS reflect important details about the mechanisms for J_{H_2O} in the mesosphere and J_{O_3} in the stratosphere.

1. **J_{H_2O} in the mesosphere:** The maximum in β_{H_2O} arises from a transition from photolysis in the L_α spectral region (121 nm) to photolysis in the Schumann-Runge band region (175-190 nm), leading to an inflection in the total J vertical profile (figure below)



Photodissociation rates for water vapor for L_α wavelengths (top) and for L_α plus the S-R band spectral region (bottom). In both plots, the solid, dashed, and dotted curves correspond to SZA values of 0° , 30° and 60° , respectively.

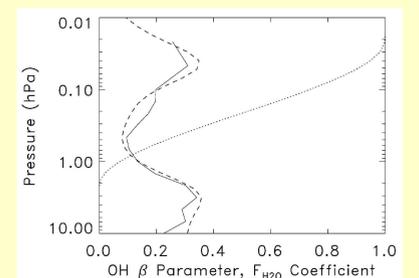
2. **J_{O_3} in the stratosphere:** The maximum in β_{O_3} results from the shape of the Hartley band cross section, and from the fact that the primary source of opacity in the spectral region is ozone itself. A shift in emphasis from the peak of the band to the wings of the band at larger optical depths leads to a temporary reduction in the steepness of the SZA dependence near 10 hPa.

3. **Contributions of J_{H_2O} and J_{O_3} to P_{HO_x} :**

If we express the production of HO_x as

$$P_{HO_x} \propto F_{H_2O} J_{H_2O} + (1 - F_{H_2O}) J_{O_3} \quad (\text{eq 4})$$

where F_{H_2O} is the fractional contribution of J_{H_2O} to the total production of HO_x , then the MLS vertical profile of β_{OH} can be used to derive the relative contributions of J_{H_2O} and J_{O_3} to HO_x production, as shown below.



Mean β_{OH} from 2004-2008 MLS OH measurements (solid) along with best-fit β_j profile using a linear combination of ozone and water vapor photodissociation raised to the power of 0.45 (dashed). Dotted curve shows derived relative contribution of water vapor photodissociation (F_{H_2O}) to the total production of HO_x .

Key Points:

- J_{O_3} controls P_{HO_x} below 0.8 hPa
- J_{H_2O} dominates P_{HO_x} above 0.1 hPa
- Magnitude of β_{OH} is consistent with $(P_{HO_x})^{0.45}$ rather than a square-root dependence, possibly a result of linear HO_x loss reactions.